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A MINERALOGICAL STUDY OF THE MOLTEN SULPHUR FILTER CAKE PRODUCED DURING THE OXYGEN PRESSURE LEACHING OF ZINC CONCENTRATE

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Silver Recovery in the Zinc Industry

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A MINERALOGICAL STUDY OF THE MOLTEN SULPHUR FILTER CAKE PRODUCED DURING THE OXYGEN PRESSURE LEACHING OF ZINC CONCENTRATE

by

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ABSTRACT

The filter cake produced by the hot filtration of the melted sulphur-sulphide flotation concentrate made from the leach residue produced during the commercial-scale oxygen pressure leaching of zinc concentrate at Cominco Ltd., Trail, B.C. has been examined chemically and mineralogically. The filter cake consists of major sulphur, sphalerite and lead jarosite together with lesser amounts of galena, chalcopyrite, pyrite, quartz and silicate gangue. After complete extraction of the elemental sulphur with CS_2, the concentration of silver in the filter cake is 382 ppm Ag. Although silver is present in the lead jarosite ($\sim$300 ppm Ag) and in the galena ($\sim$1500 ppm Ag), the amounts of these phases are inadequate to account for all the silver present. No other silver-bearing phases were detected, nor was silver detectable at the edges of the sulphide grains.

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ÉTUDE MINÉRALOGIQUE DU RÉSIDU DE FILTRATION DE SOUFRE FONDU QUI SE FORME DURANT LA LIXIVIATION SOUS PRESSION EN PRÉSENCE D'OXYGÈNE, D'UN CONCENTRÉ DE ZINC

par

J.E. Dutrizac* et T.T. Chen*

RÉSUMÉ

Le résidu qui s'accumule lors de la filtration à chaud du concentré de soufre et de sulfure fondus produit par la flottation des résidus de la lixiviation commerciale sous pression, en présence d'oxygène, d'un concentré de zinc, à l'usine de la Cominco Ltd, à Trail (C.-B.), a fait l'objet d'analyses chimiques et minéralogiques. Ce résidu se compose d'importantes quantités de soufre, de sphalérite et de jarosite de plomb, combinées à des quantités plus faibles de galène, de chalcopyrite, de pyrite, de quartz et d'une gangue silicatée. Une fois extrait le soufre élémentaire contenant du CS_2, la concentration d'argent dans le résidu est de 382 ppm. Bien que la jarosite de plomb et la galène en contiennent (~300 ppm Ag et ~1500 ppm Ag respectivement), ces quantités ne peuvent justifier de tout l'argent présent. Aucune autre source d'argent n'a été décelée, pas plus que nous avons pu détecter de l'argent à la périphérie des particules sulfurées.

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INTRODUCTION

Cominco Ltd. has installed and is operating the Sherritt oxygen pressure leach process as part of a major modernization underway at Trail, B.C. (1). About 12% of the total zinc concentrate feed processed by that company is handled in the pressure leach circuit. The horizontal autoclave in use has a published capacity of 190 tonnes of concentrate per day, and contains four separately agitated compartments with slurry overflow from compartment to compartment. The slurry is flashed to atmospheric pressure in two stages, is conditioned to promote sulphur crystallization and then is floated to remove elemental sulphur and residual sulphides. The flotation tailing consists mostly of lead jarosite together with silicate gangue and some sulphur, sulphides, etc. The elemental sulphur-sulphide flotation concentrate is melted and is filtered hot to yield a clean sulphur product and a filter cake rich in unleached sulphides that is recycled.

Most of the silver contained in the original pressure leach residue reports to the flotation tailing, but a small portion (5-10%) is recovered in the sulphur-sulphide flotation concentrate, and the silver in this portion is further concentrated into the filter cake formed during hot filtration. The filtered sulphur is virtually silver-free. A previous investigation discussed the flotation tailing and the incorporation of silver in it (2). The purpose of this study is to characterize the molten sulphur filter cake by both chemical and mineralogical means in the hope of shedding additional light on the deportment of silver, as well as that of lead, zinc, etc., during the pressure leaching of zinc concentrates.

EXPERIMENTAL

A single sample of solidified sulphur filter cake made during August, 1983 was received for study. This sample had been produced by the leaching of Sullivan zinc concentrate which typically contains 49.6% Zn, 11.2% Fe, 4.1% Pb and 32.4% S and consists principally of sphalerite, pyrrhotite and galena together with traces of chalcopyrite, pyrite, quartz and silicate gangue.

Elemental sulphur present in the supplied sample was removed by CS_2 extraction in a Soxhlet reactor. The sample ($\sim$5 g) was placed in filter paper and was refluxed several times; the liquid was drained and the CS_2 was evaporated so that elemental sulphur could be determined directly by weighing. Two consecutive extractions were performed with >99% sulphur recovery occuring in the first extraction.

In addition to classical chemical analysis of the products, the sulphur filter cake, before and after sulphur removal by Soxhlet extraction, was examined by a variety of mineralogical techniques. Polished sections were prepared and examined on a scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) and backscattered electron imagery. Some of the grains were also analyzed with a MAC 400 electron microprobe; the data were corrected using a modified version of the EMPADR VII computer program. Efforts were also made to probe the contact between the sulphide grains and the mounting medium to see if silver had been precipitated on the surface of the sulphides.

RESULTS AND DISCUSSION

General Characterization of the Sulphur Filter Cake

The as-received filter cake has the composition presented in Table 1; Soxhlet extraction indicated the presence of 33.27% S^{o}. Removal of the elemental sulphur resulted in the enrichment of the residue in metals; the enrichment factors are essentially constant, suggesting that all the metals, including Ag, remain in the residue and are not extracted with the sulphur. The silver levels measured in the sulphur filter cake are comparable to those found previously (2) in the jarosite fraction produced during the flotation of the sulphur from the leach residue (viz., 280-345 ppm Ag).

Table 1 - Chemical analyses of the filter cake before and after elemental sulphur removal

Element	As-received filter cake	Filter cake after S^{o} removal	Enrichment factor
Zn	16.91%	25.86%	1.53
Fe	5.83%	8.86%	1.52
Cu	0.79%	1.17%	1.48
Pb	4.21%	6.46%	1.53
Ag	253 ppm	382 ppm	1.51
S_{Tot}	45.48%	20.91%	-
S^{o}	33.27%	0.00%	-

Microscopic examination of the as-received filter cake (Figure 1) revealed the presence of various sulphide (white through light grey) and silicate grains (dark grey), masses of jarosite crystals (light grey) as well as elemental sulphur. The elemental sulphur was present as spherical

masses a few microns in size; it appears black in the SEM micrographs and is nearly indistinguishable from the mounting medium which also appears black. In Figure 1, the solid white grains are galena and the solid light grey particles are sphalerite, chalcopyrite or pyrite. Sphalerite is the most abundant sulphide followed by galena, chalcopyrite and pyrite. The dark grey grains are quartz or various Mg-silicates of Mg-Al-silicates. Although sphalerite, chalcopyrite and pyrite occur mostly as monominerallic, liberated grains, the galena particles are invariably rimmed with $PbSO_4$, 1-2 μm thick. Figure 2 illustrates a large galena grain (white) completely rimmed with $PbSO_4$ (very light grey). The porous-looking medium grey areas of Figure 1 (center and upper left) are masses of small jarosite crystals. The jarosite crystals are a major constituent of the sulphur filter cake and are shown in more detail in Figure 2 (light grey platelets surrounding the galena grain) and in Figure 3 (light grey, center). The individual jarosite crystals are ~1 μm thick by ~10 μm in diameter, but tend to occur in fairly large aggregates ~50 μm (Figure 1). SEM-EDX analysis showed the jarosites to be essentially zincian lead jarosite containing lesser amounts of K, Al, Cu or Si. The jarosite crystals are compositionally similar to those reported previously in the sulphur flotation tailing (2); the clusters of jarosite crystals have probably floated because of the presence of some elemental sulphur, a sulphide grain, etc. No silver was detected by SEM-EDX analysis of any of the particles present in the as-received sulphur filter cake.

The data of Table 1 suggest that the CS_2 extraction of sulphur in the Soxhlet reactor has little effect on the other constituents of the sulphur filter cake, and this assumption is supported by microscopic study of the material after sulphur removal (Figure 4). The general view is very similar to that of Figure 1, except that elemental sulphur is no longer present.

Again the bright white areas are galena grains rimmed with $PbSO_4$. The compact, light grey grains are sphalerite, chalcopyrite or pyrite, with sphalerite being the major phase. The large dark grey particles are quartz or various Mg-silicates. The medium grey masses of small crystals are zincian lead jarosite containing K, Al, Cu or Si. A few larger grains of gypsum ($CaSO_4.2H_2O$) and fine particles of $ZnSO_4$ (?) or possibly ZnS were also seen. No silver was detected in any of the particles by SEM-EDX analysis or by prolonged X-ray mapping of the sulphur-extracted filter cake.

Silver-bearing Phases

Although SEM-EDX analysis failed to detect any silver-bearing grains, this is not unexpected given the detection limit of this technique (~5,000 ppm Ag). The electron microprobe is more sensitive to silver (detection limit ~300 ppm Ag), but electron microprobe analysis of sphalerite, chalcopyrite and pyrite did not detect any silver. The galena, however, was found to be silver-bearing with silver concentrations ranging from 700 to 3,000 ppm Ag (average ~1,500 ppm Ag). Although the possibility exists for the precipitation of Ag_xS onto the surface of the sulphide particles, electron microprobe analysis of the contacts between the sulphide particles and the mounting medium did not indicate any concentration of silver. No silver whatsoever was detected on sphalerite, chalcopyrite or pyrite; silver was detected at the edges of the galena grains, but the concentrations were less than those of the galena itself, suggesting that the silver counts originated from that portion of the electron microbeam overlapping the PbS. SEM-EDX study of jarosite particles indicates them to be similar to the jarosite present in the flotation tailing (2) that contains ~300 ppm Ag. Thus, the jarosite in the sulphur filter cake likely also contains ~300 ppm Ag.

The sulphur-extracted filter cake analyzes 6.46% Pb and 382 ppm Ag, and consists of ~1/5 lead jarosite (Figures 1 and 4) although a precise quantification of the amount of jarosite present is virtually impossible given the small individual crystal sizes (1-10 μm) in the jarosite crystal aggregates. Since the lead jarosite contains ~16% Pb (2), this suggests that 3.2% Pb is present as lead jarosite and that 3.26% Pb occurs as PbS. If silver is present only in the jarosite (300 ppm Ag) and galena (1,500 ppm Ag), the anticipated silver assay of the sulphur-extracted filter cake would be:

$$0.20 \times 300 \text{ ppm} + \frac{3.26}{100\%} \times \frac{239}{207} \times 1{,}500 \text{ ppm} = 116.4 \text{ ppm Ag.}$$

If all the lead in the sulphur-extracted filter cake is present as lead jarosite (~16% Pb, 300 ppm Ag), the expected silver concentration would be:

$$\frac{6.46}{16} \times 300 \text{ ppm} = 121 \text{ ppm Ag.}$$

If all the lead is present as PbS (~1500 ppm Ag), the expected silver assay would be:

$$\frac{6.46}{100\%} \times \frac{239}{207} \times 1500 = 112 \text{ ppm Ag.}$$

The above calculations indicate that ~1/3 of the silver is present in the galena and/or lead jarosite, but that 2/3 of the total silver is still not accounted for.

CONCLUSIONS

The filter cake produced by the hot filtration of the elemental sulphur concentrate made by Cominco Ltd. in the commercial leaching operation at Trail, B.C. consists of major sulphur, sphalerite and lead jarosite,

together with lesser amounts of galena, chalcopyrite, pyrite, quartz and silicate gangue. Although silver is present in both the lead jarosite (~300 ppm Ag) and galena (~1500 ppm Ag), the amounts of these phases are such as to account for only ~1/3 of the total silver present. The major silver carrier in the molten sulphur filter cake remains undetected.

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Fig. 1 - General view of the as-received molten sulphur filter cake. (SEM backscattered electron micrograph).

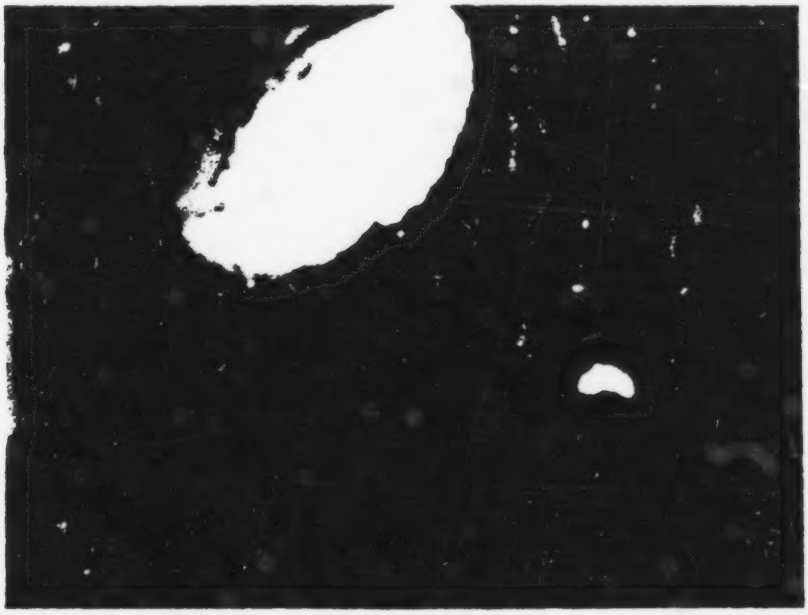

Fig. 2 - Large galena grain (white) rimmed by $PbSO_4$ (very light grey) and in contact with fine jarosite crystals (medium grey). (SEM backscattered electron micrograph.)

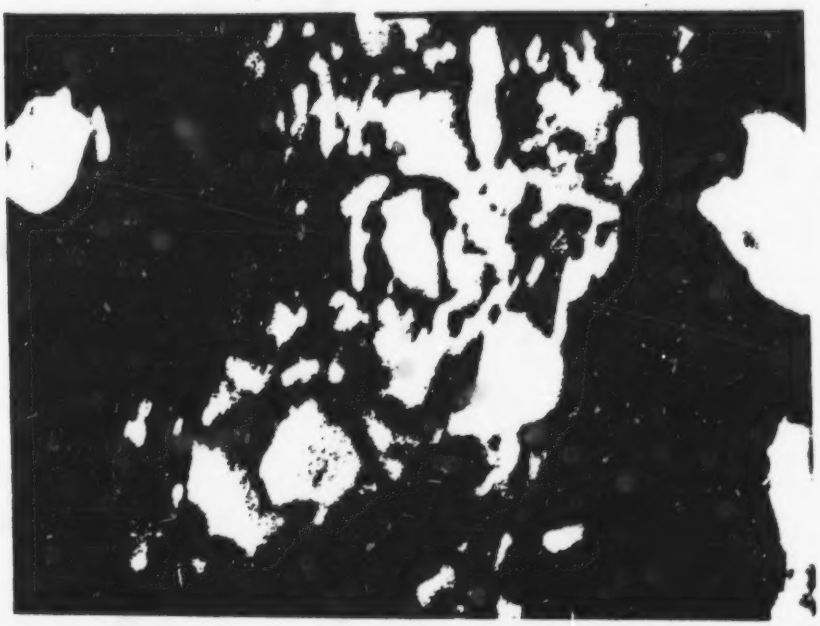

Fig. 3 - Aggregate of small lead jarosite crystals in the as-received sulphur cake. (SEM backscattered electron micrograph.)

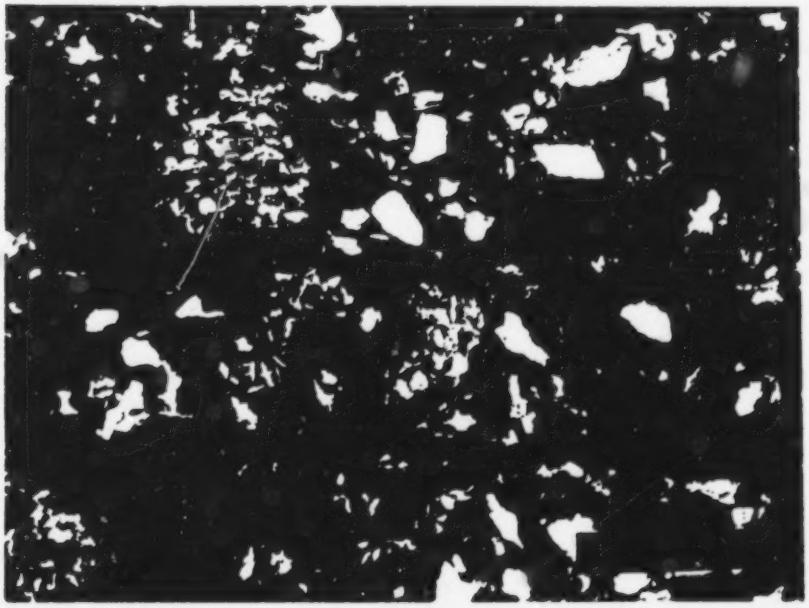

Fig. 4 - General view of the molten sulphur filter cake after the CS_2 extraction of all elemental sulphur. (SEM backscattered electron micrograph.)